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Testing various mixing rules for calculation of viscosity of petroleum blends

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ABSTRACT

Seventeen mixing rules reported in the literature used for predicting kinematic viscosity of petroleum and its fractions were examined for accuracy by comparing the estimated values with the experimental viscosities of four crude oils (21.31, 15.93, 12.42 and 9.89°API gravity) and their blends with a diluent (diesel) at several proportion. Tested mixing rules were classified as pure mixing rules, mixing rules with a *VBI* parameter, and mixing rules with an additional parameter. The results indicated a general trend to fail as the crude oil API gravity decreased, although at high temperature of analysis the predictions improved. After calculating standard errors for all predictions, only four of these rules showed acceptable accuracy (Chevron, Walther, Einstein and Power law), nevertheless no rule was capable of estimating viscosity for all the crude oils, highlighting that predicting viscosity is a challenging task. This general result led a further analysis for testing the accuracy of mixing rules in predicting viscosity for light distillates (naphtha, diesel and vacuum gas oil) and their blends; basically the same results were found, although a fifth rule (Chririnos) showed good agreement with experimental values.

1. Introduction

With the increased production of heavy and extra-heavy crude oils some physical and chemical properties have become more important than they were in the past, such as asphaltene content, viscosity and density. Viscosity and density are the most important parameters since the oil needs to have appropriate values to assure its transportation through the pipelines. Frequently, heavy crude oils with API gravity less than 15° cannot be transported without a prior reduction of their viscosity, as this type of crudes comes along with viscosities ranging from a few thousand to millions of centipoises (cP) at reservoir temperature, while 400 cP is a normal maximum desired pipeline viscosity. Hence suitable methods to reduce the viscosity are implicit in all enhanced oil recovery and transport processes.

Early investigations demonstrated that oil viscosity decreased substantially with an increase in temperature or by the addition of gaseous or liquid diluents. However, a meaningful viscosity reduction with gaseous diluents can only be accomplished at elevated pressures, while liquid diluents can dilute the viscosity at any pressure including the ambient. Therefore, the problem of high viscosity can be simply solved by mixing the oil with a diluent such as condensates, light crudes and even organic solvents, although one important disadvantage for using condensates is their availability and the possible precipitation of asphaltenes. Solvents are also injected into the reservoir for well cleaning, stimulation, fracturing, and, less frequently, for miscible displacement. Engineering application of these processes often requires calculation of mixture viscosities [1].

However, as viscosity has a molecular origin and it is highly dependent on the molecular interaction, a problem arises when trying to predict the viscosity of oil mixtures, as it behaves differently to other additive properties (i.e. molecular weight, density, impurity content). Early observations made evident that the simple linear law of mixtures was never exactly obeyed, the predicted viscosities were uniformly lower than those obtained by the mixing rule, besides, the greater the difference in the viscosities of the two components the greater the error [2]. Viscosity, consequently, does not follow linear behavior. In addition, several other variables must be taken into account, such as the dilution rate, the respective viscosities and densities of the oil and the diluents.

Various standardized methods are available for experimental determination of viscosity for different types of crudes and petroleum products, the most used are ASTM D88, ASTM D445, ASTM D2170, ASTM D7042, ASTM D7483 and ASTM E102. The major differences among them are the type and required amount of sample, the experimental setup, the time for analysis, the operating conditions of equipment and the ranges of viscosity in which the equipment can be used. In practice, it has been observed that measuring the viscosity of crude oils with low API gravity is complicated due to their own nature and difficulty to handle. This makes the analysis requires more time and greater amount of sample to obtain reliable results.

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Nomenclature

A	more viscous component
As	empirical coefficient
API	API gravity
a	viscosity interaction parameter in Eq. (11b)
a_{AB}	interaction parameter
B	less viscous component
b	constant in Eq. (18)
C	Walther constant in Eq. (10)
G_{AB}	interaction parameter
I	viscosity constant
L	viscosity function
$(\ln \nu)^E$	excess function
$(\ln \nu)^{id}$	ideal viscosity of a mixture
$(\ln \nu)_{real}$	real viscosity of a mixture
M	molecular weight
m	molar fraction; constant in Eq. (18)
N	number of data
n	viscosity reduction parameter of B in Eq. (11c); exponent in power law in Eq. (16)
R	universal gas constant
RE	relative error
RSE	relative standard error
SE	standard error
T	absolute temperature, K
V	molar volume
VBI_i	refutas and Chevron index component i
VBI_β	refutas and Chevron index of the blend
w	weight fraction
x	volume fraction
x'	compositional parameter

Greek symbols

α	empirical constant ($0 \leqslant \alpha \leqslant 1$)
β^E	excess viscosity
β^G	group contribution
β^S	structural contribution
γ_i	activity coefficient of the component i
ε	energy of bonds between the molecular in the mixture
M	dynamic viscosity, Cp
μ^{id}	ideal viscosity
ν	kinematic viscosity, cSt
ν_{AB}	interaction coefficient
ν_{io}	viscosity of the pure component i
ν_i^{calc}	calculated viscosity
$\nu_i^{\exp}$	experimental viscosity
ρ	density
$\Delta\rho$	differential density ($\rho_A - \rho_B$)
ϕ	liquid molar volume fraction

The typical viscometer used to determine the viscosity of low API gravity oils by ASTM D445 method requires 120–150 mL of sample, uses a heating bath with mineral oil to maintain a constant temperature, and takes 2–3 h for the viscosity analysis. On the contrary, the Stabinger Viscometer (ASTM D7042) is easier to handle and operate, is half the size of the conventional viscometer, $30 \times 25 \times 40$ cm, uses 2–3 mL of sample and needs only 5 min for the analysis. In addition, it provides the values of density, kinematic and dynamic viscosities at any temperature without the need of a heating bath. Its main disadvantage is the impossibility to analyze high viscosity samples such as heavy and extra-heavy crude oils. This problem can be solved by diluting the high viscosity sample with a solvent, so that the viscosity of the resulting blend can be determined. Having the viscosity of the solvent and the relative amount of samples used for blending allows, with the use of a mixing rule, for calculating the required viscosity of the original sample.

Now, the problem arises when trying to decide which mixing rule is better to use among those reported in the literature. The estimation of the viscosity of mixtures is today one of the most difficult problems in the entire domain of property estimation. The first proposed formula was developed by Arrhenius [2] in 1887, and has been the starting point for several authors [3,4]. Bingham [3] published one of the first studies regarding the theoretical and experimental bases of viscosity of binary mixtures and discarded the prevailing assumption that viscosities were additive. Kendall and Monroe [5] proposed an exponent equation based on measurements of molar fractions which was in good agreement with observed viscosities. Later, the development of more complex equations that include parameters calculated from experimental measurements improved the agreement between observed and predicted viscosities [6–11]. The prediction of viscosity for multicomponent systems has been calculated using a viscosity excess function which is computed from the structural and group contributions to account for deviation from ideality; however this method could give considerable high deviations from experimental measurements [12,13]. Various expressions have been proposed to predict viscosities of heavy oils, bitumen and petroleum fractions blends [1,14–16] finding good correlation between observed and predicted values, although some limitations were observed due to temperature dependence of the method. Al-Besharah et al. [17] compared three different methods to predict viscosity (ASTM D341 [18], Refutas index method [19] and a four-parameter model based on the Ratcliff and Khan [12] equation) finding better representation of the experimental data with the four-parameter model and the highest deviations with the Refutas index method. Dolmatov et al. [20] investigated the agreement of different empirical equations with experimental data of mixed petroleum products at various blend proportions and temperatures, the lowest errors were found with the double log Walther equation [7]. Barrufet and Setiadarma [21] developed a mixing rule based on the Lederer equation that can estimate with high accuracy the viscosity reduction of heavy oils with solvents for high viscosity ratios, at any solvent proportion and for temperatures from ambient to 450 K. Mago [22] demonstrated that neither log linear nor power law provided enough flexibility to describe the viscosity of extra heavy oil, and that it was necessary to use a new flexible mixing rule with more variables to regress to improve predictions.

As can be seen, there are various rules to calculate the viscosity of blends. However, there is not an attempt in the literature to compare all of them and decide which one is the best to be used for heavy petroleum. In this work experimental viscosities of heavy crude oils determined with the Stabinger Viscometer (ASTM D7042) were used to test several reported mixing rules in order to evaluate their accuracy for predicting the viscosity.

2. Description of mixing rules

A total of 26 mixing rules were considered in this work, although not all of them were applied for the reasons that will be discussed later. The rules were classified according to number